



PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicants: Keung, et al.

Examiner: Hai Vo

Serial No.: 09/666,928

Art Unit: 6748

Confirm. No.: 6748

Docket: 10188

Filed: September 21, 2000

For: HEAT-SEALABLE MULTI-LAYER
WHITE OPAQUE FILM

Commissioner for Patents
Washington, DC 20231

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TC 1700
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DECLARATION UNDER 37 CFR 1.132

Sir:

I, Robert A. Migliorini do hereby declare and state:

1. I am one of the inventors named in the above captioned patent application.
2. I have a bachelors degree in Chemical Engineering from Tufts University and a Masters degree in Materials Engineering and a Masters in Business Administration degree from Rochester Institute of Technology. Also, I have taken a number of courses relating to thermoplastic film technology.
3. I have worked in the Films Division of ExxonMobil Chemical Corporation (formerly Mobil Oil Corporation) for more than fifteen (15) years and have held a variety of positions in the

research and development and manufacturing groups. For the past three (3) years, I have worked in the manufacturing group and my current title is Plant Manager.

4. I have extensive knowledge in the development and manufacture of thermoplastic films and the polymeric materials and additives that are used to form such films.

5. I have read and understood the final Office Action in the above-captioned case which was mailed on February 24, 2003.

6. I am familiar with the Crimp minimum seal temperature (Crimp MST) and the testing procedure used by ExxonMobil (a copy of ASTM F88 is attached hereto as Exhibit 1). Crimp MST is the seal temperature required to provide a minimum seal strength using a controlled sealing procedure. This procedure is described in ASTM F88 and it is the industry standard for testing heat sealable films. To summarize the test procedure, samples of a heat sealable film are sealed at a fixed pressure (20 psi) and varying temperatures and then tested for seal strength. The Crimp MST is the seal temperature required to provide a minimum acceptable seal strength (200 grams/inch). In many packaging applications involving plastic films, a lower MST is required for high speed packaging applications. A packaging film with a lower MST permits packaging lines to be run at higher speeds, and hence increased productivity levels. Accordingly, it has been found to be desirable to design a plastic film with a low MST.

7. ExxonMobil's WOS-2 and WOW films are shown and described in the ExxonMobil Product Characteristics Manual, 4th Edition, published in 2000 (copies of the relevant pages are attached hereto as Exhibit 2). I am familiar with these films and I have been involved with tests that were conducted on them. The WOS-2 and WOW films are currently being marketed by ExxonMobil Chemical Company and are made in accordance with pending Claims 13 and 17, respectively. Both of these films have sealant layers which contain more than 98.5 weight percent ethylene-propylene-butylene terpolymer with a DSC (differential scanning calorimetry) melting point of about 122.5°C.

8. The ExxonMobil Product Characteristics Manual includes separate tables for the WOS-2 and WOW films (pages 89 and 45, respectively), which list the properties of the films. These tables show that the Crimp Seal MST (minimum seal strength) is approximately 180 °F (82 °C) for both films. This is significantly lower than similar film structures that I have tested. For example, I tested three samples of ExxonMobil's 40HM film which have a similar five-layer structure as the WOS2 and WOW films. The 40 HM films have substantially the same inner core and tie layers as the WOS2 and WOW films but have different outer layers. One outer layer of the 40 HM film contains high density polyethylene (Equistar M6030B) and the other outer layer contains an ethylene-propylene-butylene (EPB) terpolymer (Chisso XPM7510) with a DSC melting point of about 130°C. The minimum seal temperature (MST) was tested on the EPB

layer of the 40 HM films and the results are listed in the table below. Also listed in the table are the MST data of the EPB layer for the WOS-2 and WOW films obtained from the ExxonMobil Product Characteristics Manual.

| ExxonMobil Product No. | Description of Film | Minimum Seal Temperature (MST) |
|------------------------|---|--------------------------------|
| WOS2 | 5-layer film corresponding to Claim 13 | 180 °F |
| WOW | 5-layer film corresponding to Claim 17 | 180 °F |
| 40 HM, Sample 1 | 5-layer film w/ HDPE and EPB outer layers | 215.0 °F |
| 40 HM, Sample 2 | 5-layer film w/ HDPE and EPB outer layers | 219.2 °F |
| 40 HM, Sample 3 | 5-layer film w/ HDPE and EPB outer layers | 219.5 °F |

9. The MST test results listed in the table above show that the WOS2 and WOW films which are made in accordance with the claims of the present invention have a MST that is at least 35 °F lower than the 40 HM films. The WOS2 and WOW films, like the films of the present invention, use an EPB terpolymer having a DSC melting point of about 122.5°C. In contrast, the 40 HM films use an EPB terpolymer having a DSC melting point of about 130°C. It

is my opinion that at least part of the reason for the significantly lower MST is attributed to the use of an ethylene-propylene-butylene terpolymer with a lower DSC melting point in the sealant layer. *

10. The pending claims in the present application have a core layer that comprises a polypropylene homopolymer of high stereo-regularity. These films also have a high crystallinity since crystalline polymers are distinguished by a highly regular molecular structure. High crystallinity is inherent in a polypropylene homopolymer of high stereo-regularity.

11. The relationship between high stereo-regularity and high crystallinity is well known to those of ordinary skill in the art of polymer films and is described in most text books relating to polymer structures. For example, McCrum et al., *Principles of Polymer Engineering*, Oxford University Press 1988 (copies of the relevant pages are attached hereto as Exhibit 3) states at p. 19:

What is the molecular characteristic which distinguishes the crystalline polymers from non-crystalline? It is, to be brief, **molecular regularity**: an irregular molecular structure prevents crystallization.

12. The relationship between high stereo-regularity and high crystallinity is also described in Odian, *Principles of Polymerization*, John Wiley & Sons (copies of the relevant pages are attached hereto as Exhibit 4) at p. 580:

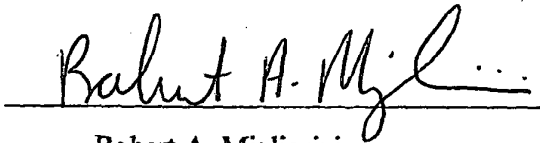
Application Serial No. 09/666,928

Docket: 10188

The regularity or lack of regularity in polymers affects their properties by way of large differences in their abilities to crystallize. . . The ordered structures are capable of being packed into a crystal structure while unordered structures are not.

13. I hereby declare that all statements made herein are of my own knowledge and are true, and that all statements made on information and belief are believed to be true; and further that the statements have been made with the knowledge that wilful false statements and the like so made are punishable by fine or imprisonment, or both, under § 1001 of Title 18 of the United States Code and that such wilful false statements may jeopardize the validity of any patent issuing on the present invention.

Dated: April 18, 2003


Robert A. Migliorini

171611_1

Crimp seal strength, MST, and range

ExxonMobil # 490
ASTM F 88

Definition

Crimp seals, which are produced at controlled conditions of jaw design, temperature, pressure, and dwell, are measured in terms of force required to open the seam. The following properties are calculated and reported.

- **Crimp seal strength** is the maximum force to peel open a seal made at specified conditions. Units are g/in or g/2.5 cm.
- **Crimp minimum sealing temperature** (Crimp MST) for a specified pressure and dwell, is the temperature (°F or °C) required to achieve a certain minimum strength seal. ExxonMobil has standardized with 200 g/in as the seal strength for minimum acceptable performance. Other values may be more appropriate for particular applications.
- **Seal range** is the difference between the maximum and minimum temperatures that will produce an adequate seal at a specified pressure and dwell. Units are °F or °C.

Relevance to performance

The strength of a seal is important to package integrity, and many end-users specify a minimum requirement.

Crimp MST and seal range are important, because they predict packaging machine efficiency and productivity. A lower MST corresponds to a wider seal range and, therefore, a wider operating window. This means that the packaging line will produce acceptably sealed packages even when the speed is ramping up and down, or when there is variation in jaw temperature. On the other hand, a higher MST and narrower seal range forces the packager to control these variables better, or else packages can be rejected for weak, open seals, or distorted seals.

What determines a film's seal properties

A film's sealing surface is a coated or coextruded layer. The sealing properties can be impacted by several factors:

- Formulation of sealant layer (resin and additive recipe)
- Thickness of sealant layer
- Total thickness of the film (With thicker films, it takes longer for heat to transfer from the sealing jaws to the sealing surfaces than it does with thinner films. Therefore, both the effective sealing temperature and the resulting seal strength are lower.)
- Bond strength of sealant layer to adjacent layer
- Contamination (An otherwise good-sealing surface may not seal well if additives from a laminating web transfer onto it, or if dust/fines are trapped in the seal area.)
- Surface treatment, including backside treatment, can damage sealability

Seal properties are a key design criteria when developing a sealable film. In production, these properties are regularly measured to make sure that the formulation or process has not shifted.

Test principles

In order to compare sealing properties among different films, ExxonMobil uses a set of standard conditions for producing heat seals. They are summarized in Table 12.

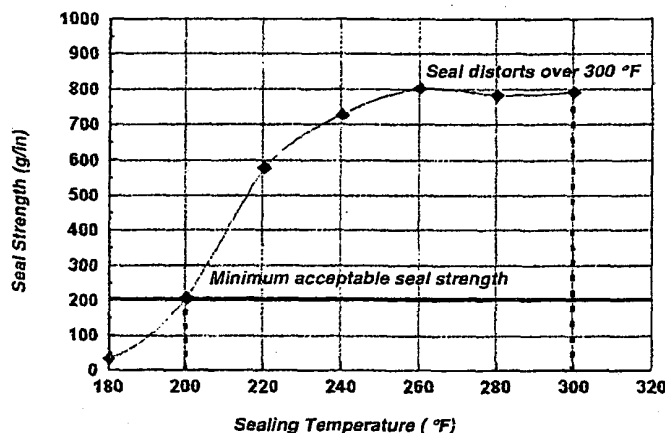
| Condition | Description |
|----------------|---|
| Sealing device | Wrap-Ade Crimp Sealer Model J or K, modified with new PID temperature controllers |
| Jaw design | Vertically serrated crimps |
| Temperature | Both jaws are heated and desired set point is controlled to + 2°F (1°C) |
| Pressure | 20 psi (1.4 bars) |
| Dwell | ¼ sec |

Table 12: ExxonMobil conditions for producing test crimp seals

After a test seal has been produced, its strength can be measured with a tensile tester or a Suter tester. ExxonMobil typically uses the simpler Suter tester, which pulls the seal apart at 12 in/min and records peak force.

ASTM and ExxonMobil test procedures have similarities and differences. Unlike ExxonMobil, the scope of ASTM test procedure F 88 is only the measuring of the force to open the seal, not the making of the seal at a set of standard conditions. ASTM specifies the use of a tensile tester, while ExxonMobil uses a Suter tester. The 12 in/min pull rate of ExxonMobil is within the ASTM-defined a rate of 10 to 12 in/min.

It is often desirable to produce seals at a series of temperatures, measure the seal strengths, and develop a seal curve that looks like in Graph 3.



Graph 3: Typical seal curve

Crimp Seal Strength is defined at a particular temperature, or as the average for a range of temperatures. For the seal curve represented in Graph 3, the following properties can be derived.

$$\text{Seal Strength at } 260^{\circ}\text{F (SS}_{260\text{F}}) = 800 \text{ g/in}$$

$$\text{SS}_{260 - 300\text{F}} = 790 \text{ g/in}$$

$$\text{Minimum Sealing Temperature for a 200 g/in seal (MST}_{200\text{g}}) = 200^{\circ}\text{F (93}^{\circ}\text{C)}$$

$$\text{MST}_{500\text{g}} = 217^{\circ}\text{F (103}^{\circ}\text{C)}$$

$$\text{Seal Range (SR)} = \text{Maximum} - \text{Minimum Sealing Temperature}$$

$$\text{SR}_{200\text{g}} = 300 - 200 = 100^{\circ}\text{F (56}^{\circ}\text{C)}$$

$$\text{SR}_{500\text{g}} = 300 - 217 = 83^{\circ}\text{F (46}^{\circ}\text{C)}$$

The horizontal red line denotes a minimum acceptable seal strength of 200 g/in. It intersects the seal curve at 200°F (93°C), so this is the MST_{200g}. If you know that the minimum acceptable seal strength is another value, the same curve may be used to determine the corresponding MST and seal range. For example, 500 g/in seals occur at 217°F (103°C), so this is the MST_{500g}.

Most OPPs will distort at temperatures above 300°F (149°C), if dwell time is in excess of ½ second or so. Therefore, this value is used as the maximum sealing temperature. The difference between the maximum and minimum sealing temperatures is equal to the seal range.

CAUTION: Seal data can not be compared when the seals are produced on different equipment or at different conditions.

Related terminology

ASKCO sealer

The ASKCO sealer is a laboratory heat sealer that ExxonMobil uses for process control of coated films. It has nine separate temperature-controlled, one-side heated, low-pressure, flat-sealing stations. The multiple stations allow a whole seal curve to be generated from one sealed film strip.

Sentinel sealer

The Sentinel sealer is a common laboratory heat sealer in the flexible packaging industry. Like the ASKCO sealer, it is a one-side heated, flat sealer. Unlike the ASKCO, there are no multiple stations, so it can only make a seal at one temperature at a time. ExxonMobil does not use this sealer. Data generated with the Sentinel sealer, by other companies, can not be compared with ExxonMobil data.

Failure mode

Failure mode refers to how the seal fails as it is being pulled apart. A "peel" failure means that the films separated without tearing. A "delamination" failure is a type of peel failure where the material separates between two adjacent layers, rather than at the sealing interface. (For example, a printed extrusion lamination can fail between the ink and poly layers, because they formed a weak bond.) Finally, a "tear" failure means that the film tears as the seal is being pulled apart. This suggests that the seal and the bonding between layers are stronger than the film.

Suter tester

Suter tester is a device specifically designed to measure peak seal strengths. It is simpler and speedier than using a tensile tester. Suter testers are not commercially available.

ExxonMobil

Flexible Packaging Films

Product Characteristics Manual

4th Edition

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OPpalyte®

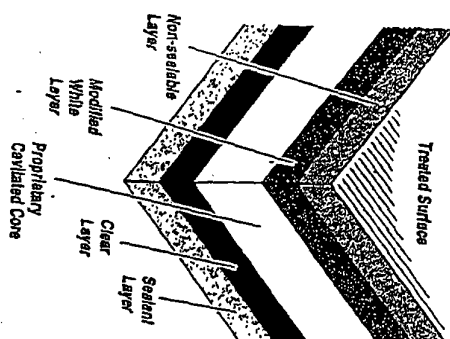
Developmental WOS-2

Description

OPpalyte WOS-2 is a one-side treated, one-side sealable, white opaque OPP film with a proprietary cavitated core. WOS-2 was developed to provide performance improvements over 278 WOS in terms of lower and more consistent COF, lower MST, and improved print performance.

Key Performance Characteristics

- Outstanding opacity
- Superior machinability
- ◆ Heat seal range of approximately 120°F (65°C)
- ◆ Average seal strengths over 500 g/in (500 g/2.5 cm)
- Bright white appearance



Available Optical Gauges

| Product | Gauge (mil) | Gauge (micron) | Yield (in ² /lb) | Yield (m ² /kg) |
|-----------|-------------|----------------|-----------------------------|----------------------------|
| 278 WOS-2 | 1.80 | 46 | 27,600 | 89.5 |

Typical Uses

- Extrusion Lamination
- Adhesive Lamination
- Unsupported
- ◆ LEVULIN/PEWOS-2
- ◆ SPV-L/Ink/AdhesiveWOS-2
- ◆ Ink/278 WOS-2
- ◆ Plain 278 WOS-2 (HFFS, Multilam, or VFFS)

Important Considerations

- 1 WOS-2 was developed and designed for frozen novelty applications. The stiffness, slip characteristics, and sealability of WOS-2 have been optimized to provide outstanding performance on multi-lane equipment.
- 2 WOS-2 can be used in VFFS applications.
- 3 WOS-2 contains a non-migratory slip package for excellent machinability and hot slip without compromising appearance or seals. **DO NOT RETREAT.**
- 4 WOS-2 should be printed for extrusion laminations or when laminating with high-barrier PVC to ensure consistent adhesion.

- 5 WOS-2 may need to be printed when surface printing with water-based inks.
- 6 WOS-2 is lap sealable to coextruded films.

Properties

| Preliminary Property Values | | | |
|--|------------------------------|--------------|-----------|
| Property | Units | Test Proc. # | 278 WOS-2 |
| Optical Gauge | mil | nominal | 1.80 |
| | micron | nominal | 46 |
| | in ² /lb | | 27,600 |
| Yield | in ² /kg | | 86.5 |
| | lb/in | | 15.5 |
| | g/in | | 66.0 |
| Tensile Strength | lb/in | | 510 |
| | lb/in | | 510 |
| | lb/in | | 510 |
| Dimensional Stability | % change | | 4.30 |
| | % change | | 4.30 |
| | % change | | 4.0 |
| COF | | | 430 |
| Gloss (45°) | lf | | 442 |
| WVTR @ 100°F (38°C), 90% RH | g/100 in ² /24 hr | | 518 |
| Light Transmission | % | | 488 |
| Crimp Seal Strength @ 210°F, 20 psi, % sec | g/in | | 490 |
| Crimp Seal MST @ 99°C, 1.4 bars, 7.5 s | g/2.5 cm | | 490 |
| Crimp Seal MST to achieve a 200 g/in seal | °F | | 490 |
| | °C | | 490 |

Product information on these facing pages is subject to the qualifying statements on page ii of this book.

Developmental WOS-2

ExxonMobil

89

OPPalyle®

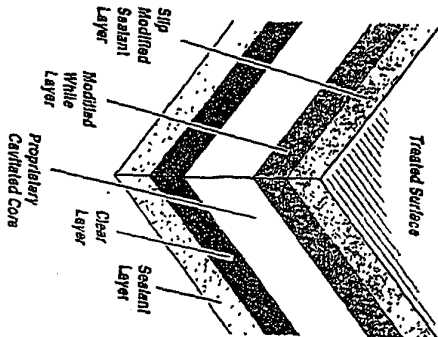
Developmental WOW

Description

OPPalyle WOW is a one-side treated, two-side sealable, white opaque OPP film with a proprietary cavitated core. This film is designed for HFFS and overwrap applications.

Key Performance Characteristics

- Outstanding opacity
- Bright white appearance
- Superior machinability
- Low and stable COF
- Heat seal range of approximately 120°F (65°C)
- Excellent print performance for flexo graphic and rotogravure printing
- Peelable seal for ice cream sandwich applications



Available Optical Gauges

| Product | Gauge (mil) | Gauge (micron) | Yield (lb/7lb) | Yield (m ² /kg) |
|---------|-------------|----------------|----------------|----------------------------|
| 35 WOW | 1.40 | 35 | 35,400 | 50.3 |
| 45 WOW | 1.80 | 45 | 27,800 | 38.5 |

Typical Uses

Adhesive Lamination

• SPW-L/MI/Adhesive/WOW

Unsupported

• InLWOW
• Plain WOW (Overwrap)

Important Considerations

- WOW was developed and designed for frozen novelty applications. This film's stiffness, slip characteristics, and sealability have been optimized to provide outstanding performance for ice cream sandwich applications.
- WOW can be used in VFFS applications.
- WOW contains a non-migratory slip system for excellent machinability and hot slip without compromising appearance or seals. DO NOT RETREAT.

- WOW should be primed for extrusion laminations or when laminating with high barrier PVC to ensure consistent adhesion.
- WOW is lap sealable to coextruded films.

Properties

| Property | Units | Test Proc. # | 35 WOW | 45 WOW |
|------------------------------------|------------------------------|--------------|--------|--------|
| Preliminary Property Values | | | | |
| Optical Gauge | mil | nominal | 1.40 | 1.80 |
| | mil | actual | 35 | 45 |
| Yield | lb/7lb | | 35,400 | 27,800 |
| | m ² /kg | | 50.3 | 38.5 |
| Unit Weight | lb/in ² | | 12.2 | 16.5 |
| | g/m ² | | 18.9 | 26.3 |
| Light Transmission | % | | 24 | 24 |
| Crimp Seal Strength | g/in | | 480 | 300 |
| • 240°F, 20 psi, 3 sec | | | | |
| • 116°C, 1.4 bars, 75 sec | | | | |
| Crimp Seal MIST | °F | | 480 | 180 |
| to achieve a 200 g/in seal | | | | |
| Tensile Strength | MD | | 510 | 18 |
| | TD | | 510 | 2.8 |
| | MD | | 510 | 26 |
| | TD | | 510 | 4.6 |
| Dimensional Stability | % change | | 4.5 | 4.5 |
| • 276°F (135°C) | | | | |
| COF | U/T | | 430 | 32 |
| Gloss (45°) | U | | 442 | 80 |
| WVTR @ 100°F (38°C), 90% RH | g/100 in ² /24 hr | | 518 | 43 |
| Opacity | % | | 518 | 6.7 |
| | | | 488 | 82 |

White Films

Principles of Polymer Engineering

N. G. McCrum

*Department of Engineering Science
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OXFORD UNIVERSITY PRESS

New York Tokyo

1988

18 Structure of the Molecule

The entire network will consist of chains of A units meeting at B cross-links as indicated in Fig. 1.6. The proportion of B will, of course, determine the tightness of the cross-linked network. The polymerization of other cross-linked networks of importance in rubber and in reinforced plastic technology is described in Chapters 3 and 7. Note that cross-linked networks can be produced by reactions involving already synthesized linear polymers (as in the case of the cross-linking of polyethylene (see Fig. 1.2) and in the vulcanization of rubber (see Fig. 0.1)).

1.6 MOLECULAR SYMMETRY AND THE TENDENCY TO FORM CRYSTALS

For some mechanical properties, crystalline polymers have distinct advantages over the polymeric glasses which do not crystallize. This is particularly true in respect of toughness and ductility; amorphous polymers will not form useful fibres. As an example, consider polyethylene, which at room temperature is partially crystalline. The crystals are extremely thin and have the form of lamellae (see Fig. 1.7). Those portions of the molecule which have not



Fig. 1.7. Lamellae within adjacent bands of a banded spherulite of linear polyethylene crystallized at 125°C. The specimen was cut open after crystallization, and lamellae are revealed by permanganic etching of the cut surface. The electronmicrograph is of a carbon replica of the etched cut surface (after D.C. Bassett). Scale bar = 10 μ m.

1.6 Molecular Sy

crystallized are trapped between involving a high-modulus crystalline fraction, intimately mixed with the amorphous fraction, leads to good ductility and to

What is the molecular character of polymers from the non-crystalline irregular molecular structure

- One form of regularity is condensation polymers
- A source of irregularity is irregularity in the size and packing of the molecule
- Another form of irregularity

Crystallization can be disrupted

The three forms of symmetry illustrated by the model in Fig. 1.4 are shown out for inspection in a planar zig-zag form. The placement of the X atoms (a) the X atoms fall all on one side (b) the X atoms alternate regularly (c) arranged randomly. These three forms are syndiotactic (b), and atactic (c) be stated that crystals are:

- always formed from the
- sometimes formed from
- never formed from the

Note that there is no change in the position of the atom X. The pioneering work on isotactic, crystalline vinyl polymers was awarded the Nobel Prize for

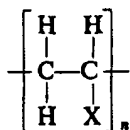
The tremendous significance demonstrated best by polypropylene, an abundant monomer. It is of the isotactic form using Ziegler-Natta catalysts. Fig. 1.4) exerts an influence on

1.6 Molecular Symmetry and the Tendency to form Crystals 19

crystallized are trapped between the lamellae. It is this two-phase structure, involving a high-modulus crystal fraction and a low-modulus rubbery amorphous fraction, intimately interconnected in a sandwich structure, that leads to good ductility and toughness.

What is the molecular characteristic which distinguishes the crystalline polymers from the non-crystalline? It is, to be brief, **molecular regularity**: an irregular molecular structure prevents crystallization.

- One form of regularity is the ABABA sequence which is mandatory for condensation polymers such as the nylons (§1.3).
- A source of irregularity is random side branching as in polyethylene; irregularity in the size and placement of the side branches inhibits the packing of the molecule into the crystal.
- Another form of irregularity can occur in the vinyl polymers.



Crystallization can be disrupted by the asymmetry introduced by the atom X.

The three forms of symmetry (or **stereo-regularity**) of vinyl polymers are illustrated by the model in Fig. 1.8. To facilitate comparison, each model is laid out for inspection in a planar zig-zag, so that it is straight and not in a crumpled form. The placement of the X atom is then seen to take one of three patterns. In (a) the X atoms fall all on one side of the plane in which the carbon atoms lie; in (b) the X atoms alternate regularly from side to side; in (c) the X atoms are arranged randomly. These three configurations are termed **isotactic** (a), **syndiotactic** (b), and **atactic** (c). Of these three forms of stereo-regularity it can be stated that crystals are:

- always formed from the isotactic polymers;
- sometimes formed from the syndiotactic; and
- never formed from the atactic.

Note that there is no change in chemical composition, merely in the placement of the atom X. The pioneering work in the recognition and polymerization of isotactic, crystalline vinyl polymers is due to Ziegler and Natta who were awarded the Nobel Prize for Chemistry in 1963:

The tremendous significance of the phenomenon of stereo-regularity is demonstrated best by polypropylene (X is CH₃). Propylene is a cheap and abundant monomer. It is of interest only when polymerized in the isotactic form using Ziegler-Natta catalysis. The surface structure of the catalyst (see Fig. 1.4) exerts an influence on the presentation of the monomer to the growth

20 Structure of the Molecule

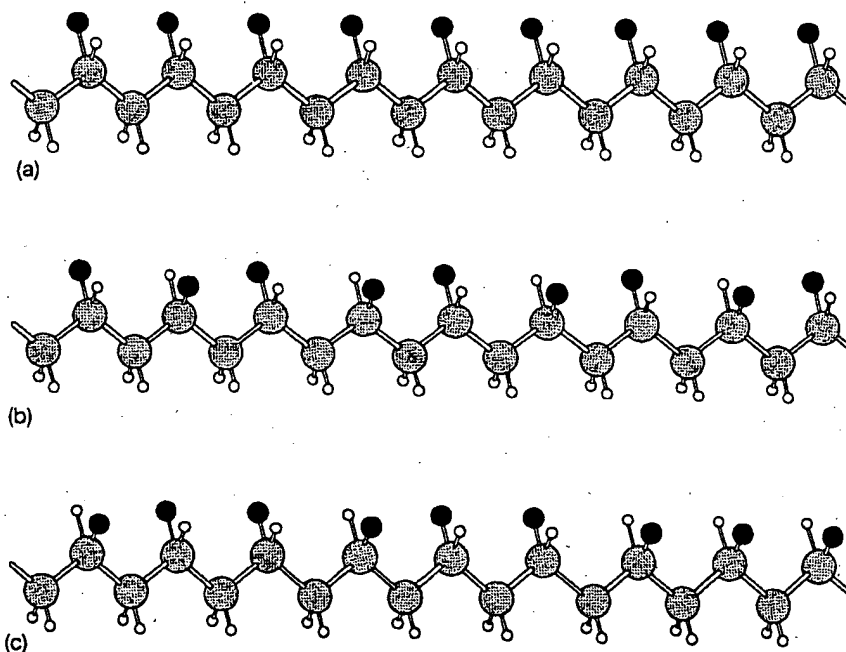


Fig. 1.8. Stereoregularity in a vinyl polymer: three different molecular configurations (a) isotactic, (b) syndiotactic, and (c) atactic. The molecular shape may be changed from this planar zig-zag by rotation around C-C bonds. This will change the conformation of the molecule; it does not change the configuration, which is established at the instant of polymerization.

point. This leads to an ordered reaction producing the isotactic polymer. The catalyst is never perfect, so a small fraction of atactic polymer is produced simultaneously.

1.7 DISTRIBUTION OF RELATIVE MOLECULAR MASS

The size of a molecule is described most directly by n (structures (II-IV, IX, XII)), which is known as the degree of polymerization. Of more use operationally is the relative molecular mass, formerly termed the molecular weight. The term relative molecular mass[†] has been slow to gain acceptance, possibly because of its unwieldy length; we will abbreviate it to RMM. RMM has no units, being a pure number (it is a ratio between masses). Thus for molecule Y

$$\text{RMM} = \frac{\text{mass of molecule Y}}{(1/12) \text{ mass of an atom of carbon 12}}$$

[†] The term relative molar mass is identical to relative molecular mass.

$$= \frac{1}{(1/12)}$$

A polyethylene molecule of RMM

since the RMM of carbon neglects the insignificant el

After polymerization, it i molecules with many differ intimately mixed. For exce they may be separated into value of RMM. The mecha (see Fig. 1.9). The rapid dr values typical of the paral quantifies the common ex chemical structure of the p

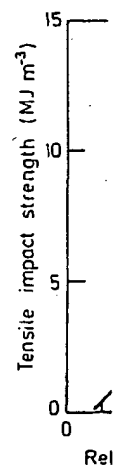


Fig. 1.9. Effect of RMM on normal polymer with a distrib each fraction had a particular was measured. The tensile im quantifies the common exper a polyethylene with less than with a toughness incomparab S. P. E. Conference Proceedi

Principles of — Polymerization —

SECOND EDITION

George Odian

*Professor of Chemistry
The College of Staten Island
The City University of New York
Staten Island, New York*

A WILEY-INTERSCIENCE PUBLICATION

JOHN WILEY & SONS

New York / Chichester / Brisbane / Toronto / Singapore

those in which there is a *cis* configuration of the polymer chain bonds entering and leaving each ring; the *threo* structures have a *trans* configuration of the polymer chain bonds entering and leaving the rings.

8-2 PROPERTIES OF STEREOREGULAR POLYMERS

8-2a Significance of Stereoregularity in Polymers

The occurrence of isomerism in polymers plays a major role in their practical utilization. There are very significant differences in the properties of unordered and ordered polymer structures as well as in ordered polymers of different types (i.e., syndiotactic vs isotactic and *cis* vs *trans*). The ordered polymer structures are dramatically different from the corresponding unordered structures in terms of their physical properties. This is especially interesting in terms of polymers which are ordered due to chiral centers. Chirality has a much greater effect on the properties of polymers (biological as well as synthetic) than on the properties of small molecules.

8-2a-1 Isotactic, Syndiotactic, and Atactic Polypropylenes

The regularity or lack of regularity in polymers affects their properties by way of large differences in their abilities to crystallize. Atactic polymers are amorphous (noncrystalline), soft ("tacky") materials with little or no physical strength. On the other hand, the corresponding isotactic and syndiotactic polymers are usually obtained as highly crystalline materials. The ordered structures are capable of being packed into a crystal structure while unordered structures are not. Crystallinity leads to high physical strength and increased solvent and chemical resistance as well as differences in other properties which depend on crystallinity. A prime example of the commercial utility of stereoregular polymers is polypropylene. Atactic polypropylene is essentially useless, while *isotactic* is a high melting, strong, crystalline polymer, which finds large-scale use as both a plastic and fiber [9,18]. The annual United States production of *isotactic* polypropylene is about four billion pounds.

Isotactic polypropylene like polyethylene has a good combination of properties: excellent chemical and solvent resistance, high electrical and stress-crack resistance, and high strength. It is among the lightest (0.90 g/ml) of all commercial plastics and has a very high strength-to-weight ratio. The high melting temperature of 181°C allows *isotactic* polypropylene to be used at temperatures above those where high density polyethylene is no longer adequate. *Isotactic* poly(1-butene) and poly(4-methyl-1-pentene) are becoming commercially important because they possess higher melting temperatures than polypropylene.

While the properties and utility of isotactic polymers have and are being extensively studied, those of syndiotactic polymers have received very little attention.

Properties of Stereoregular

The reason is the relative polymerizations that yield centered compared to the polypropylene, the proportionate extent [19]. *Syndio* crystallized. However, cry (about 20°C) and is more the polypropylene.

8-2a-

Geometrical isomerism in the properties of the *cis* are due to symmetry: the same as for small molecules in the *cis* and *trans* utilization. Thus, *cis*-1,4-structures, and is an excellent at temperatures. About used in the United States sands, and other typical order, much less rubber significant crystallinity. 5 golf balls and for electric game occurs in both the the *Hevea brasiliensis* tree as the major naturally o the double bonds in the used commercially is th America and Malaya, yi the *trans* isomer.

ity and *trans*-1,4-Polypropenes, the *cis* polymer pounds produced annual

Table 8-1

| Polymer |
|-------------------|
| 1,4-Polybutadiene |
| 1,4-Polyisoprene |

^aData from [20]

Chemistry of Polymerization

chain bonds entering and configuration of the polymer

POLYMERS

Polymers

major role in their practical properties of unordered and structures of different types (i.e. polymer structures are different in terms of their structures in terms of their properties of polymers which are different effect on the properties of small molecules

Polypropylenes

Their properties by way of polymers are amorphous physical strength. On the polymers are usually structures are capable of being structures are not. Crystalline and chemical resistance on crystallinity. A primary polymers is polypropylene is a high melting, strong plastic and fiber [9,18] polypropylene is about four

combination of properties and stress-crack resistance commercial plastics and glass temperature of 180°C above those where high (1-butene) and poly(4 t because they possess

ive and are being extensively used very little attention

Properties of Stereoregular Polymers

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The reason is the relative ease of formation of isotactic polymers; stereospecific polymerizations that yield syndiotactic structures are much less frequently encountered compared to those that yield isotactic structures. However, in the case of polypropylene, the properties of the syndiotactic polymer have been studied to some extent [19]. Syndiotactic polypropylene, like the isotactic structure, is easily crystallized. However, crystalline, syndiotactic polypropylene has a lower T_m (by about 20°C) and is more soluble in ether and hydrocarbons than crystalline, isotactic polypropylene.

8-2a-2 cis- and trans-1,4-Poly-1,3-Dienes

Geometrical isomerism in 1,4-poly-1,3-dienes results in significant differences in the properties of the cis and trans polymers. The trans isomer crystallizes to a greater degree due to symmetry and has higher T_m and T_g values (Table 8-1). These trends are the same as for small molecules such as the cis- and trans-2-butenes. The differences in the cis and trans polymers leads to major differences in their properties and utilization. Thus, cis-1,4-polyisoprene has very low crystallinity, low T_m and T_g values, and is an excellent elastomer over a wide temperature range, which includes ambient temperatures. About two billion pounds per year of cis-1,4-polyisoprene are used in the United States for tires, coated fabrics, molded objects, adhesives, rubber bands, and other typical elastomer applications. trans-1,4-Polyisoprene is a much harder, much less rubbery polymer since it has relatively high T_g and T_m values and significant crystallinity. Small amounts of this polymer are used in manufacturing golf balls and for electrical cable covering. It is interesting to note that 1,4-polyisoprene occurs in both the cis and trans forms in nature. Hevea rubber, obtained from the *Hevea brasiliensis* tree (in Brasil, Sri Lanka, Indonesia, Malaya) and other plants, is the major naturally occurring 1,4-polyisoprene. It contains more than 98% of the double bonds in the cis configuration. (Over 80% of all cis-1,4-polyisoprene used commercially is the natural Hevea rubber.) Other trees, mostly in Central America and Malaya, yield gutta percha or balata rubber, which is predominantly the trans isomer.

cis- and trans-1,4-Polybutadienes are produced commercially. As with the polyisoprenes, the cis polymer is by far the more important with close to one billion pounds produced annually.

Table 8-1 Crystalline and Glass Transition Temperatures^a

| Polymer | Isomer | T_g (°C) | T_m (°C) |
|-------------------|--------|------------|------------|
| 1,4-Polybutadiene | cis | -102 | 1 |
| | trans | -58 | 141 |
| 1,4-Polyisoprene | cis | -73 | 28 |
| | trans | -58 | 74 |

^aData from [20].